

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/234840438>

Evaluation of Granular Activated Carbon, Shale, and Two Organoclays for Use as Sorptive Amendments in Clay Landfill Liners

Article in *Journal of Geotechnical and Geoenvironmental Engineering* · July 2005

DOI: 10.1061/(ASCE)1090-0241(2005)131:7(848)

CITATIONS

49

READS

165

4 authors:



Shannon L. Bartelt-Hunt

University of Nebraska at Lincoln

132 PUBLICATIONS **2,049** CITATIONS

[SEE PROFILE](#)



James Albert Smith

University of Virginia

149 PUBLICATIONS **3,331** CITATIONS

[SEE PROFILE](#)



S. E. Burns

Georgia Institute of Technology

73 PUBLICATIONS **1,355** CITATIONS

[SEE PROFILE](#)



Alan J. Rabideau

University at Buffalo, The State University of New York

77 PUBLICATIONS **846** CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Integrated decision support for urban land use, green infrastructure, and stormwater management [View project](#)



Water and Health in Limpopo [View project](#)

Evaluation of Granular Activated Carbon, Shale, and Two Organoclays for Use as Sorptive Amendments in Clay Landfill Liners

Shannon L. Bartelt-Hunt¹; James A. Smith²; Susan E. Burns³; and Alan J. Rabideau⁴

Abstract: Four materials with high sorptive capacities for organic compounds [granular activated carbon (GAC), shale, benzytriethylammonium-bentonite (BTEA-bentonite), and hexadecyltrimethylammonium-bentonite (HDTMA-bentonite)] were evaluated for their use in compacted clay landfill liners by conducting laboratory sorption and permeability experiments with both a 0.002 N CaSO₄ solution (to simulate the ionic strength of ground water) and a synthetic leachate. Results from equilibrium sorption experiments with 0.002 N CaSO₄ indicate that all four amendments have a very high sorptive capacity for the three organic solutes tested: benzene, trichloroethylene, and 1,2-dichlorobenzene. GAC exhibited the highest sorptive capacity for all three solutes, followed by BTEA-bentonite, HDTMA-bentonite, and shale. Experiments conducted with synthetic leachate indicate that GAC and BTEA-bentonite did not exhibit competitive sorption effects with the synthetic leachate constituents, while shale did exhibit some competitive sorption effects between benzene and trichloroethylene and the synthetic leachate constituents. Permeability tests conducted on specimens composed of Ottawa sand, untreated bentonite, and either 3 or 9% amendment by weight were also performed. Results indicate that all amended specimens had a hydraulic conductivity less than or equal to 1×10^{-7} cm/s, with the exception of the specimen amended with 3% GAC, which had a measured conductivity value of 2×10^{-7} cm/s. Changing the permeant fluid to a synthetic leachate had little effect on the overall conductivity of the specimens. One-dimensional benzene transport simulations were performed to more completely evaluate how effective these materials would be if incorporated into a compacted clay liner. Simulations indicated that all proposed amendments would effectively retard the transport of benzene through the liner. Amending liners with 3 or 9% GAC or 3 or 9% BTEA-bentonite effectively eliminated benzene flux through the liner over a 100-year period. Liners amended with HDTMA-bentonite or shale also reduced the benzene flux exiting the liner over the simulation period, but to a lesser extent.

DOI: 10.1061/(ASCE)1090-0241(2005)131:7(848)

CE Database subject headings: Shale; Activated carbon; Sorption; Permeability; Leaching; Benzene; TCE; Clay liners.

Introduction

Leachates from municipal solid waste (MSW) and hazardous waste disposal facilities have been found to contain a wide range of potential environmental contaminants, including volatile organic compounds. A recent U.S. Environmental Protection Agency (EPA) report characterizing landfill leachates from over 200 MSW landfills found organic compounds, such as benzene, toluene, ethylbenzene, and methylene chloride, in over 50% of

the leachate samples tested (U.S. EPA 2000). In order to protect underlying ground-water resources from these and other pollutants, waste disposal sites are commonly lined with clay and geomembrane composite liners. For the most part, the design of these liner systems has focused on minimizing the flow rate of leachate through the liner. However, even with hydraulic conductivities less than 10^{-7} cm/s, the mass flux of many organic pollutants across earthen and intact geomembrane liners by diffusion can be significant (Shackelford 1991; Mott 1992; Park and Nibras 1993; Gullick 1998). An additional contribution to pollutant mass flux across landfill liners is made as a result of regularly occurring defects in geomembranes, either within the geomembrane itself, or within the seams between geomembrane sections.

Due to the inability of composite landfill liners to impede diffusive transport, enhancement of the sorption capacity of earthen liner materials should be considered as a means to improve liner performance. The magnitude of organic pollutant sorption to natural soils and clays is related to the organic solute's aqueous solubility and the organic-carbon content of the sorbent (Smith et al. 1988; DiCesare and Smith 1994; Chiou 1998). Because natural soils and clays typically have organic-carbon contents less than 0.5%, pollutants such as chlorinated solvents and gasoline-range hydrocarbons (with solubilities greater than a few mg/L) do not sorb appreciably. By contrast, strongly hydrophobic organic contaminants (e.g., polychlorinated biphenyls, polycyclic aromatic

¹Postdoctoral Research Associate, Dept. of Civil, Construction, and Environmental Engineering, North Carolina State Univ., Raleigh, NC 27695.

²Associate Professor, Dept. of Civil Engineering, Univ. of Virginia, Charlottesville, VA 22904 (corresponding author). E-mail: jas9e@virginia.edu

³Associate Professor, Dept. of Civil Engineering, Univ. of Virginia, Charlottesville, VA 22904.

⁴Associate Professor, Dept. of Civil, Structural, and Environmental Engineering, SUNY-Buffalo, Buffalo, NY 14260.

Note. Discussion open until December 1, 2005. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on May 6, 2004; approved on December 12, 2004. This paper is part of the *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 131, No. 7, July 1, 2005. ©ASCE, ISSN 1090-0241/2005/7-848-856/\$25.00.

hydrocarbons, etc.) and many heavy metals bind strongly to natural soils and clays.

A method of enhancing organic pollutant sorption and thus minimizing the flux of leachate pollutants through earthen liners is to amend the liners with materials capable of strongly sorbing organic pollutants. Several proposed amendments include organophilic bentonites, activated carbon, and shale (Bierck and Chang 1994; Smith and Jaffé 1994; Gullick and Weber 2001). In some cases, sorption capacities are four or five orders of magnitude greater for these materials than for natural soils and clays. Increasing the sorption capacity of the earthen liner effectively reduces the pollutant advection velocity and the rate of solute diffusion during transient solute transport without requiring an increase in liner thickness. Although a sorbed pollutant will eventually desorb from the liner, the mass flux from the bottom of the liner should be significantly reduced when an organobentonite, shale, or activated carbon is a component of the liner. In order to evaluate the potential effectiveness of sorptive materials as amendments to clay liners, sorption and permeability testing was performed on four materials: benzyltriethylammonium-bentonite (BTEA-bentonite), hexadecyltrimethylammonium-bentonite (HDTMA-bentonite), shale, and granular activated carbon (GAC). One-dimensional transport modeling was performed to determine how effective each of these amendments would be at retarding the transport of organic contaminants if incorporated into a clay landfill liner.

The use of sorptive materials in barrier systems has been suggested previously by other researchers, however this study is the first to provide an in-depth side-by-side comparison of a variety of different sorbent materials using both experimental analysis and mathematical simulations. In addition, this study provides new information on the sorption capacity and permeability of all four amendments in the presence of a complex landfill leachate.

Methods and Materials

Sorptive Materials

The two organoclays evaluated for potential use in liner systems were HDTMA-bentonite and BTEA-bentonite. These organophilic bentonites were synthesized from a naturally occurring sodium bentonite that was treated with either HDTMA-bromide $[(CH_3)_3NC_{16}H_{33}Br]$ or BTEA-chloride $[(C_2H_5)_3NCH_2C_6H_5Cl]$. Both compounds were obtained from Aldrich Chemical Company (St. Louis, Missouri), had a chemical purity of 99%, and were used as received.

The HDTMA-bentonite was synthesized at an organic cation loading corresponding to 80% of the cation-exchange capacity of the base bentonite while the BTEA-bentonite was synthesized with a loading corresponding to 50% of the cation-exchange capacity. These percentages have been shown to result in the maximum sorptive capacity for a number of volatile organic compounds (Bartelt-Hunt et al. 2003). Details concerning the method used to synthesize the organoclays have been described previously (Bartelt-Hunt et al. 2003).

Activated carbon, the third amendment proposed for evaluation, is a generic term for a variety of products composed primarily of elemental carbon that have been treated (activated) to enhance their surface areas (Manes 1998). GAC was chosen for this study since previous studies have shown that powdered activated carbon may be transported through soil-bentonite systems under the application of hydraulic gradients (Bierck and Chang 1994).

Table 1. Chemical and Physical Properties of Organic Solutes

Compound	Molecular weight (g/mol)	Solubility (mg/L)	log K_{ow}
		25°C	
1,2-dichlorobenzene	147.00	148	3.34–3.55
Trichloroethylene	131.39	1,100	2.29–3.30
Benzene	78.11	1,750	1.56–2.20

Note: All values taken from *Groundwater Chemicals Desk Reference*, 2nd Ed. (Montgomery 1996).

The GAC used in this study was a granular reactivated carbon (GAC-840R) obtained from American Norit, Inc. (Atlanta, Georgia) with a mesh size of 8×40 and was used as received.

The final sorbent evaluated was shale, a sedimentary rock formed naturally from silt and clay. The shale used in this study was carbonaceous shale obtained from Ward's Geology (Rochester, New York). The shale was ground and the portion passing a No. 40 sieve was used in experimental testing.

Conventional liner materials were represented in this study by untreated bentonite and Ottawa sand. The bentonite clay was composed of 3.6% sand, 7.3% silt, and 89.1% clay. The exchangeable inorganic cation on the base bentonite clay was primarily sodium. The Ottawa sand (Grade F-25) was obtained from U.S. Silica Company (Berkeley Springs, West Virginia) and was used as received.

Solutes

Sorption testing was performed for three relatively water-soluble organic pollutants: trichloroethylene (TCE), 1,2-dichlorobenzene (1,2-DCB), and benzene. These solutes were chosen because they are common ground-water pollutants and their solubilities make them relatively mobile in natural porous media. Physical and chemical properties of these solutes are presented in Table 1.

Synthetic Leachate

In order to accurately evaluate the sorption and permeability characteristics of these amendments for use in clay liner systems, sorption and permeability experiments were performed with both a 0.002 N $CaSO_4$ solution and a synthetic MSW leachate as the solvent phase. The synthetic leachate was used to determine how the sorption and permeability properties of the amendments would change when subjected to a complex heterogeneous mixture containing many of the chemical constituents found in actual landfill leachates. The composition of the synthetic leachate is presented in Table 2.

This composition was based primarily on a U.S. EPA report that includes characterization data from more than 200 MSW landfills in the United States (U.S. EPA 2000). The synthetic leachate composition in this study includes six of the most commonly measured inorganic and organic analytes. The concentrations of inorganic cations and anions in the synthetic leachate were chosen to correspond to the mean concentrations published in the report as closely as possible.

Heavy metals are not included in the proposed synthetic leachate although they have been measured at low concentrations in analyses of actual leachate. Any effect on sorption and permeability due to low concentrations of heavy metals will likely be overshadowed by the high concentrations of inorganic ions already present in the synthetic leachate such as calcium, magnesium, and iron.

Table 2. Composition of Proposed Synthetic Leachate

Inorganics
126 mg/L Mg^{2+}
914 mg/L Cl^-
92 mg/L Fe^{2+}
334 mg/L SO_4^{2-}
262 mg/L K^+
197 mg/L Na^+
74 mg/L Ca^{2+}
Organics
5 mg/L acetone
60 μ g/L 1,2-dichloroethane
3.5 mg/L methyl isobutyl ketone
45 mg/L phenol
20 μ g/L methylene chloride
1.5 mg/L toluene

The measured pH value of the synthetic leachate was 5.8 ± 0.3 and the measured conductivity value was 2.7 ± 0.2 mS/cm. These values agree with reported pH and conductivity values for landfill leachates, which range between 4.5 to 9 and 2.5 to 35 mS/cm, respectively (Christensen et al. 2001).

Sorption Isotherms

Sorption of TCE, 1,2-DCB, and benzene to the four proposed amendments was quantified using a conventional batch equilibration technique (Smith and Jaffé 1994; Smith and Galan 1995). Varying amounts of sorbent, 0.002 N $CaSO_4$ solution or synthetic leachate, and ^{14}C -labeled solute were combined in 15 mL glass centrifuge tubes with Teflon-lined caps. The mass of sorbent was 0.5 g for BTEA-bentonite and 2.0 g for HDTMA-bentonite; these masses were chosen to insure that 30 to 90% of the added solute was sorbed at equilibrium.

After equilibration, the reactors were centrifuged at 2,400g for 60 min at 22°C. 500 μ L of the supernatant was transferred to 5 mL of scintillation cocktail in a 7 mL scintillation vial. The radioactivity was quantified with a Packard 1900TR liquid scintillation analyzer and the measured radioactivity was related to aqueous concentration by a standard curve. The sorbed concentration of the solute in each batch reactor was then calculated by difference. For each isotherm experiment, three additional batch reactors were prepared for quality assurance. These reactors were used to quantify solute losses caused by processes other than sorption to the sorbent (e.g., volatilization, sorption to Teflon, etc.) and to quantify the background radiation and to determine if the sorbent, water, or reactor was contaminated with radioactivity.

Kinetic sorption experiments were performed to determine the time required for the three proposed solutes to reach equilibrium with the shale and activated carbon. 24 h is considered to be sufficient time for the two organobentonites to reach equilibrium, as Deitsch et al. (1998) have shown previously that sorption of carbon tetrachloride and 1,2-DCB to three organobentonites was found to be very rapid, with equilibrium occurring within the first few hours of solute-sorbent contact time. Results of kinetic testing indicated that sorption to GAC reaches equilibrium in 24 h, with the majority of uptake occurring in the first 30 min. Equilibrium sorption to shale was determined to have occurred after 48 h of solute-sorbent contact.

Table 3. Composite Soil Samples Used in Permeability Testing

Sample	Ottawa sand (wt %)	Bentonite (wt %)	Amendment type and percent
1	90	10	None
2	87	10	3% GAC
3	81	10	9% GAC
4	87	10	3% HDTMA-bentonite
5	81	10	9% HDTMA-bentonite
6	87	10	3% BTEA-bentonite
7	81	10	9% BTEA-bentonite
8	87	10	3% shale
9	81	10	9% shale

Note: GAC=granular activated carbon; HDTMA-bentonite=hexadecyltrimethylammonium-bentonite; and BTEA-bentonite=benzyltriethylammonium-bentonite.

Permeability Testing

Permeability tests were performed on specimens composed of Ottawa sand, untreated bentonite, and sorptive amendment at different weight percentages for two different permeant fluids, 0.002 N $CaSO_4$ solution and the synthetic leachate. Permeability testing was also done on core composed of Ottawa sand and untreated bentonite, which were used to represent conventional clay liner materials. The composition of each of the nine specimens tested is given in Table 3. Relatively low weight percentages of amendment (0, 3, and 9%) were chosen for investigation as it is likely cost prohibitive to use sorptive amendments at weight percentages greater than 9–10% due to their significantly increased cost over conventional liner materials. In addition, conventional bentonite has historically been added in small percentages to native soils to reduce the permeability of barrier systems. Similarly, we chose to investigate the effect of a small addition of sorptive amendment on the contaminant transport and permeability characteristics of the overall liner. The permeability of compacted soil specimens was measured with a changing-head permeability test using flexible-wall permeameters according to ASTM D5084. The optimal moisture content was determined for each soil specimen prior to permeability testing. The specimen was composed of three layers that were compacted in a compaction mold by 25 drops of a 2.3 kg hammer from a height of 40 cm at a moisture content that was 2% greater than optimal. The specimen was extruded from the compaction mold and trimmed to a length of 6.5 cm.

Compacted specimens were placed in the permeameter (Trautwein Soil Testing Equipment Co.) and back-pressure saturated by the permeant fluid at a pressure of 193 kPa for 48 h. After the core was saturated, a pressure gradient was induced by reducing the outflow pressure. The pressure difference between the inflow and outflow ends of the sample ranged from 6.8 to 27.6 kPa. The pressure differential was kept as low as possible while still allowing for completion of a permeability test within a reasonable period of time (8–12 weeks). The confining cell pressure in all experiments was 206.8 kPa. Bladder accumulators were used for storage of the leachate at the inflow and outflow ends of the core to prevent damage to the panel boards by the organic components of the leachate.

Permeability experiments were completed when three criteria were met: (1) results of three consecutive permeability determinations over a two-week period were within $\pm 25\%$ of their mean; (2) the ratio of the inflow rate to the outflow rate for the specimen was between 0.75 and 1.25; and (3) a plot of permeability versus

time showed no distinct rising or falling trend. When these criteria were met, the mean of the final three permeability measurements was averaged and recorded. At the completion of the test, the porosity, bulk dry density, and bulk density of the specimen was determined gravimetrically. Permeability tests with 0.002 N CaSO₄ as the permeant fluid were performed in triplicate. Permeability tests with synthetic leachate as the permeant fluid were first permeated with the calcium sulfate solution. After the specimen was brought to equilibrium with the calcium sulfate solution, the synthetic leachate was introduced into the specimen. Once one pore volume of leachate had passed through the specimen, the final permeability of the specimen was determined using stopping criteria outlined above. Duplicate permeability experiments were performed with synthetic leachate as the permeant fluid.

Transport Modeling Simulations

The experimental results from the sorption and permeability experiments were used as input data for transport simulations in order to evaluate the potential benefit of using sorptive amendments as a component of compacted clay liners. The *MOUSER* model (Rabideau 2003) was used to evaluate benzene transport over a 100-year period through a hypothetical 0.6 m thick liner comprised of each of the compositions listed in Table 3.

The *MOUSER* model simulates transient one-dimensional solute transport through low-permeability materials using the advection-dispersion-reaction equation, assuming equilibrium sorption:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b}{n} \frac{\partial S}{\partial t} \quad (1)$$

where C =contaminant concentration in the dissolved phase; t =time; x =distance from the domain entrance; v =fluid velocity in the x direction; D =dispersion coefficient (includes hydrodynamic dispersion and molecular diffusion); ρ_b =bulk density; n =porosity; and S =sorbed phase concentration.

Although the assumption of equilibrium sorption is not strictly valid, an approach incorporating nonequilibrium sorption was outside the scope of this study. In addition, it is likely that any effects due to nonequilibrium sorption may be minimized in an actual barrier system due to the long residence time of the contaminant within the porous media (Rabideau and Khandelwal 1998).

In all simulations, the upper boundary condition was considered as a finite-mass boundary condition, expressed as

$$C(0,t) = C_0 - \frac{1}{H_f} \int_0^t \left[v C(0,\xi) - D \frac{\partial C}{\partial x}(0,\xi) \right] d\xi \quad (2)$$

where C_0 =initial concentration in the mixing zone; and H_f =mixing-zone height in the x direction. In these simulations, C_0 =10 mg/L and H_f =0.3 m; the maximum leachate height allowed by regulation. This boundary condition represents a declining source of contaminant mass within the landfill and is considered to be more realistic than assuming a constant contaminant concentration at the surface (Rowe and Booker 1985). The lower boundary condition was set as a constant contaminant concentration of 0 mg/L. This lower boundary condition was chosen as it represents a conservative scenario for diffusion-dominated transport whereby the concentration gradient across the domain is at a maximum. The initial contaminant concentration within the domain was $C_0=0$ mg/L.

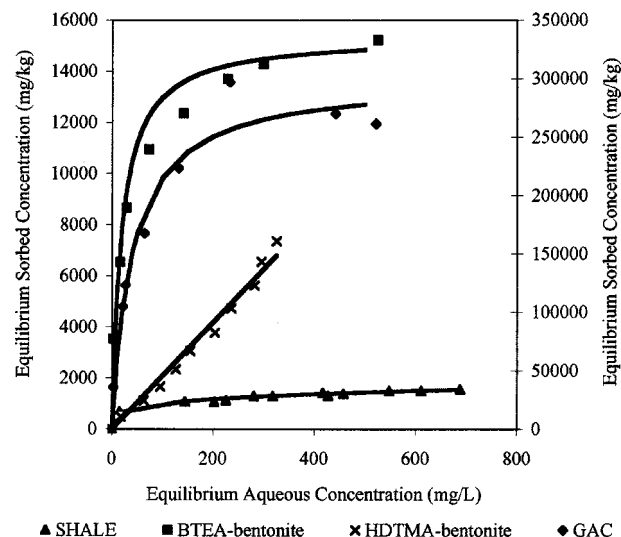


Fig. 1. Equilibrium sorption isotherms for benzene for all four sorbents with 0.002 N CaSO₄ as the solvent phase

Values for ρ_b and n were determined from the results of laboratory permeability testing. Fluid velocity (v) was determined from the hydraulic gradient ($i=1.5$) and experimentally determined values of K and n . The dispersion coefficient (D) was determined using a free-water diffusion coefficient value of 1×10^{-5} m²/d (Montgomery 1996) and a longitudinal dispersivity equal to 0.1. A diffusion hindrance parameter (H_p) was calculated for each case using the equation:

$$H_p = n^{-0.33} \quad (3)$$

Khandelwal et al. (1998) found that this relationship produced conservative estimates for effective diffusion coefficients for organic solutes in soil-bentonite slurry walls.

Parameter values determined from the best-fit isotherm models for sorption of benzene to each of the sorptive materials were used to determine the sorptive capacity of a liner system composed of sand, bentonite, and the sorptive amendment. It has been shown that the contribution to the overall sorptive capacity of a composite liner for each component can be described by multiplying the mass fraction of the component times the isotherm expression for that component. Further details of this method may be found in Smith and Jaffé (1994).

Results and Discussion

Equilibrium Sorption Isotherms

Results from sorption experiments with benzene, TCE, and 1,2-DCB as the solutes and 0.002 N CaSO₄ as the solvent phase can be seen in Figs. 1–3. Recovery in all isotherm experiments was greater than 95%. In general, GAC had the highest sorptive capacity for all solutes, followed by BTEA-bentonite, HDTMA-bentonite, and shale.

The mechanisms of sorption to each of the proposed amendments vary. Sorption to activated carbon is generally thought to occur by a physical adsorption process, and is characterized by competitive nonlinear isotherms (Manes 1998). In this study, organic solute sorption to GAC was nonlinear and characterized by a Langmuir isotherm model of the form:

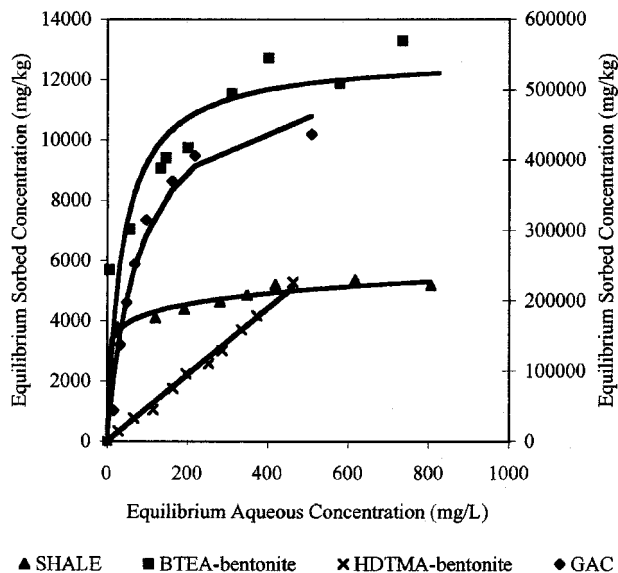


Fig. 2. Equilibrium sorption isotherms for trichloroethylene for all four sorbents with 0.002 N CaSO₄ as the solvent phase

$$C_s = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where C_s =equilibrium sorbed concentration; b and q_m =isotherm parameters; and C_e =equilibrium aqueous solute concentration. Sorption of all three solutes to BTEA-bentonite was also nonlinear and characterized by a Langmuir isotherm model. Previous research has shown that when an organoclay has an exchanged quaternary ammonium cation with benzyl, phenyl, and/or relatively short-chain alkyl functional groups (ethyl or methyl functional groups), sorption is characterized by competitive nonlinear isotherms with no clear solubility dependence (Smith et al. 1990). Based on these observations, the mechanism of sorption has been attributed to a physical adsorption process.

Uptake of benzene and TCE by HDTMA-bentonite was linear and was characterized by an isotherm of the form:

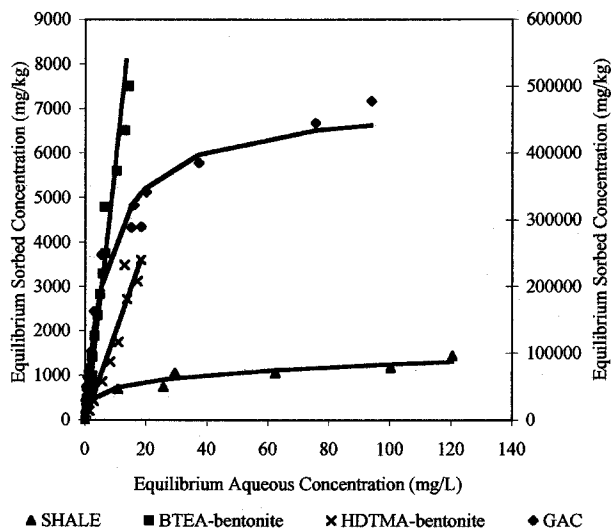


Fig. 3. Equilibrium sorption isotherms for 1,2-dichlorobenzene for all four sorbents with 0.002 N CaSO₄ as the solvent phase

$$C_s = K_d C_e \quad (5)$$

where K_d =sorption distribution coefficient. Isotherm data for sorption of 1,2-DCB to HDTMA-bentonite were slightly concave up. These sorption data were fit with a Freundlich model of the form:

$$C_s = K_f C_e^{n_f} \quad (6)$$

where K_f =Freundlich distribution coefficient; and n_f =Freundlich exponent. All HDTMA-bentonite isotherms were linear or slightly concave up, supporting the theory that sorption to clays modified with cations with long alkyl chains, such as HDTMA, occurs primarily by a partition process between the aqueous solution and the organic medium created by the alkyl chains (Smith et al. 1990). The slight upward concavity observed in some of the HDTMA-bentonite isotherm data has been observed by previous researchers and has been attributed to the formation of a discrete solute phase on the surface of the clay (Jaynes and Boyd 1991). Isotherm models were fit using a model calibration program, *ISOFIT*, using an equal data-weighting scheme (Matott 2004). All three isotherm models were fit to each set of experimental data, and the model resulting in the best fit (determined by highest R^2 value and lowest standard error of the regression) was chosen. Resulting isotherm model parameters and regression statistics are given in Table 4.

Since adsorption is the most likely mechanism for solute uptake by GAC, shale, and BTEA-bentonite, it is possible that these sorbents may exhibit some degree of competitive sorption when the solvent phase in the isotherm experiments is changed to synthetic leachate, which contains low-level concentrations of a variety of organic compounds. Quantifying the degree of competitive sorption in the presence of a landfill leachate containing a variety of organic compounds is important in evaluating the ability of these materials to retard the movement of a specified target compound through a clay liner. The presence of competitive sorption was determined by comparison of the isotherm data of the target organic solute with 0.002 N CaSO₄ as the solvent phase to the isotherm data with synthetic leachate as the solvent phase for each solute/sorbent combination (Fig. 4). In Fig. 4, isotherm data are plotted in a linearized form. Both BTEA-bentonite and GAC exhibited no competitive sorption effects for any of the three organic solutes tested when the solvent phase was changed to the synthetic leachate. Shale did exhibit significant competitive sorption for benzene and TCE, but minimal competitive effects were seen for 1,2-DCB.

The reason why competitive sorption effects were observed only 1,2-DCB on the shale and not for any of the organic solutes on either the BTEA-bentonite or GAC is not entirely known, but we hypothesize that it may be due to the surface area of the different sorbents. The surface area of each sorbent was measured using a multipoint BET method (Gemini 2360 surface area analyzer, Micromeritics) with N₂ as the adsorbate. Surface areas of 709.10, 28.65, and 11.33 m²/g were measured for GAC, BTEA-bentonite, and shale, respectively. GAC and BTEA-bentonite have a very large specific surface area compared to shale, indicating that there are a greater number of potential sorption sites on the surface of these two materials compared to shale. It is possible that no competitive sorption effects were exhibited by these two materials because both the target solute and the organic compounds in the landfill leachate sorbed to only a fraction of the potential sorption sites on the surface of these two materials. Shale did exhibit competitive sorption effects because sorption of the target organic solute occupied a large number of

Table 4. Isotherm Model Parameters for Sorption of Three Organic Solutes to Four Sorptive Amendments

Sorbent	Solute	Model	Model parameters	R^2	Standard error of the regression
Granular activated carbon	Benzene	Langmuir	Q_m (mg/kg)=229,768 b (L/mg)=0.0254	0.970	20,200
	TCE	Langmuir	Q_m (mg/kg)=536,053 b (L/mg)=0.0124	0.984	22,900
	1,2-DCB	Langmuir	Q_m (mg/kg)=476,395 b (L/mg)=0.1350	0.970	27,300
BTEA-bentonite	Benzene	Langmuir	Q_m (mg/kg)=14,942 b (L/mg)=0.0495	0.984	755
	TCE	Langmuir	Q_m (mg/kg)=12,776 b (L/kg)=0.0263	0.903	1,500
	1,2-DCB	Langmuir	Q_m (mg/kg)=7,525 b (L/kg)=0.0222	0.978	347
HDTMA-bentonite	Benzene	Linear	K_d (L/kg)=20.85	0.986	323
	TCE	Linear	K_d (L/kg)=11.04	0.994	126
	1,2-DCB	Freundlich	K_f (L/kg)=170.0 $n=1.16$	0.98	Not available
Shale	Benzene	Freundlich	K_f (L/kg)=351 $n=0.227$	0.988	48
	TCE	Freundlich	K_f (L/kg)=2,539 $n=0.110$	0.990	178
	1,2-DCB	Freundlich	K_f (L/kg)=411 $n=0.242$	0.945	116

Note: TCE=trichloroethylene; 1,2-DCB=1,2-dichlorobenzene; BTEA-bentonite=benzyltriethylammonium-bentonite; and HDTMA-bentonite=hexadecyltrimethylammonium-bentonite.

the available sites on the surface of the shale. When competing organic compounds in the landfill leachate were introduced to the system, a fewer number of sites were available for sorption of the target solute. This resulted in the shale having a decreased sorption capacity for target solutes compared to the binary-solute system. In theory, GAC and BTEA-bentonite have a finite number of surface sorption sites. It is possible that competitive sorption effects would be observed for these materials as well if the leachate had a larger effective organic concentration. In addition, there may be a unique interaction between 1,2-DCB, the organic species in the synthetic leachate, and the surface sites on the shale that contributes to the observed competitive sorption phenomena, but that cannot be directly determined from the experimental analysis.

Sorption of benzene, TCE, and 1,2-DCB to all amendments was much greater than for conventional liner materials. Sorption isotherms for the untreated bentonite and Ottawa sand had a slope of zero—indicating no measurable sorption occurred to these materials.

Permeability Testing

Results from permeability tests with 0.002 N CaSO_4 as the permeant fluid are given in Table 5. All amended specimens met or exceeded the hydraulic conductivity requirement of 1×10^{-7} cm/s stipulated by the U.S. EPA for materials used in landfill liners, with the exception of the specimen amended with 3% GAC which had a measured conductivity of 2×10^{-7} cm/s. The specimens amended with shale had the lowest conductivity, followed by specimens amended with BTEA-bentonite and HDTMA-bentonite. Specimens amended with GAC had the high-

est and most variable conductivity. The total porosity of the specimens ranged from 0.37 to 0.53, and a general decrease in porosity was observed between the 3 and 9% amendment levels for all four amendments. An exception occurred for specimens amended with GAC, which had a measured porosity of 0.48 at the 3% amendment level and 0.53 at the 9% amendment level. This increase in porosity may be due to the high internal porosity of the GAC, resulting in a greater overall porosity for specimens composed of a larger weight percentage of this material.

Results from permeability experiments with synthetic leachate as the permeant fluid may be seen in Table 6. In general, conductivity was either unchanged or decreased slightly when the permeant fluid was changed from the 0.002 N CaSO_4 solution to the synthetic leachate. These results are similar to results from a previous study that found that MSW leachate had little effect on the hydraulic conductivity of compacted clays (Quigley et al. 1988).

Hydraulic conductivity (K) is a function of the intrinsic permeability (k) of the soil and two fluid properties: Density (ρ) and viscosity (η):

$$K = k \left(\frac{\rho g}{\eta} \right) \quad (7)$$

Viscosity and density measurements made for both the 0.002 N CaSO_4 solution and the synthetic leachate indicated that these two properties did not vary significantly between the two fluids. This indicates that any measured change in conductivity is a function of a change in the intrinsic permeability of the specimen and not due to a variation in permeant fluid properties. Intrinsic permeability can be described as a function of porosity (n) and effective

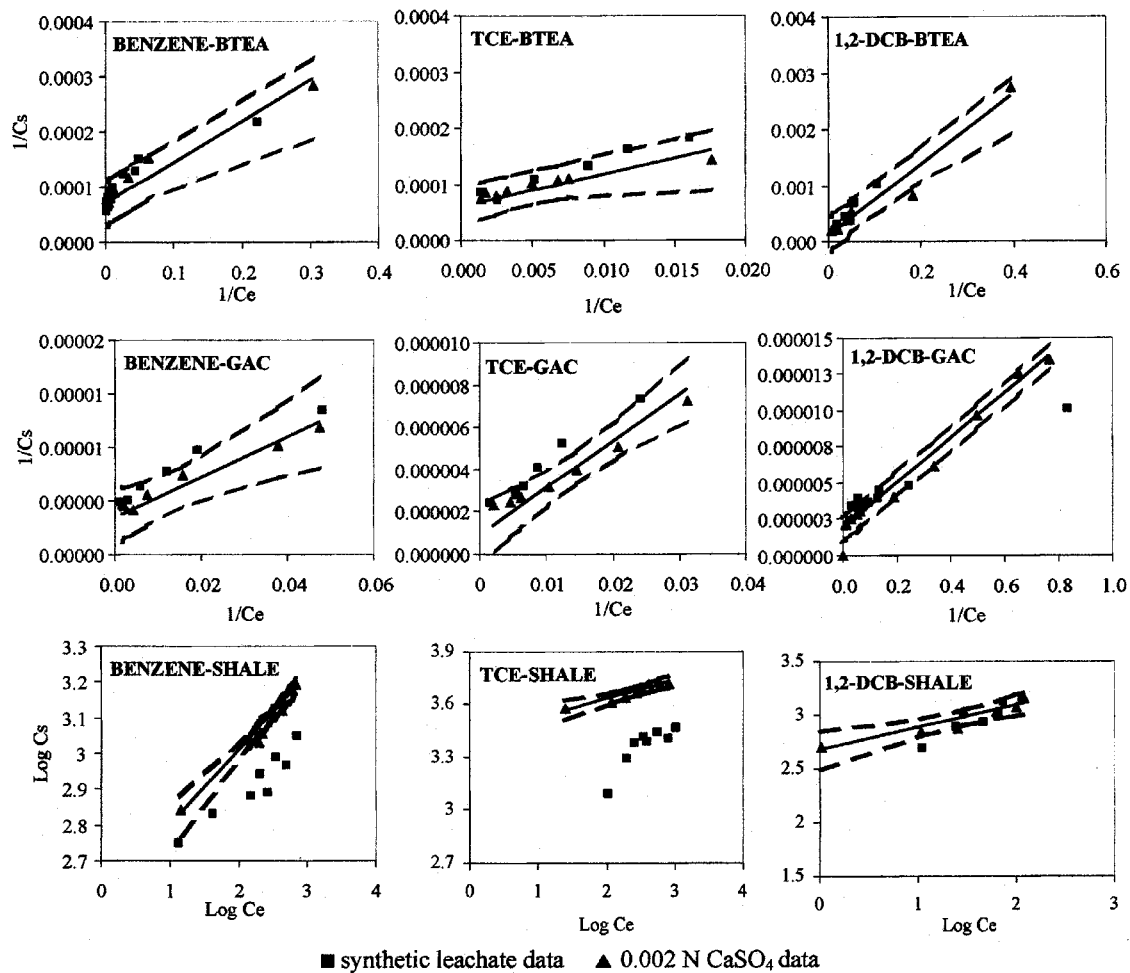


Fig. 4. Comparison of competitive sorption isotherms (solvent phase=synthetic leachate) and single-solute isotherms (solvent phase=0.002 N CaSO_4) for benzene, trichloroethylene, and 1,2-dichlorobenzene to benzyltriethylammonium-bentonite, granulated activated carbon, and shale

pore radius (r_e) (Rakhshandehroo et al. 1998) where:

$$k = nr_e^2 \quad (8)$$

The average porosity of the specimens did not change significantly when the permeant fluid was changed to the synthetic leachate. This indicates that the measured decrease in permeability is a function of a decrease in the effective pore radius resulting

from interactions between the leachate and the soil materials.

Analysis of the permeability testing results conducted with 0.002 N CaSO_4 and the synthetic leachate indicate that the incorporation of GAC, shale, or organoclay amendments will have no adverse effect on the overall permeability of compacted clay liners below landfills, and in fact, may actually serve to decrease the permeability of a liner system. The decrease in permeability as-

Table 5. Results from Permeability Experiments with 0.002 N CaSO_4 as the Permeant Fluid

Amendment type	Hydraulic conductivity (cm/s)		Bulk density (g/cm ³)		Dry bulk density (g/cm ³)		Porosity		Number of replicates
	Ave.	Std. error	Ave.	Std. error	Ave.	Std. error	Ave.	Std. error	
No amendment	1×10^{-7}	2×10^{-8}	2.20	0.02	1.73	0.01	0.47	0.01	5
3% GAC	2×10^{-7}	8×10^{-8}	2.09	0.01	1.62	0.01	0.48	0.01	3
9% GAC	1×10^{-7}	7×10^{-8}	2.15	0.07	1.62	0.05	0.53	0.02	3
3% HDTMA-bentonite	4×10^{-8}	1×10^{-8}	2.37	0.05	1.86	0.04	0.50	0.02	3
9% HDTMA-bentonite	7×10^{-8}	3×10^{-8}	2.13	0.01	1.74	0.01	0.39	0.01	3
3% BTEA-bentonite	1×10^{-8}	2×10^{-9}	2.15	0.03	1.76	0.01	0.40	0.01	3
9% BTEA-bentonite	1×10^{-8}	2×10^{-9}	2.13	0.01	1.74	0.01	0.38	0.01	3
3% shale	2×10^{-8}	4×10^{-9}	2.20	0.01	1.79	0.01	0.41	0.01	3
9% shale	3×10^{-9}	8×10^{-10}	2.14	0.02	1.76	0.01	0.37	0.01	3

Note: Ave.=average; Std. error=standard error; GAC=granular activated carbon; HDTMA-bentonite=hexadecyltrimethylammonium-bentonite; and BTEA-bentonite=benzyltriethylammonium-bentonite.

Table 6. Results from Permeability Experiments with Synthetic Leachate as the Permeant Fluid

Amendment type	Ave. hydraulic conductivity (cm/s)	Ave. bulk density (g/cm ³)	Ave. dry bulk density (g/cm ³)	Ave. porosity
No amendment	2×10^{-8}	2.17	1.73	0.45
3% GAC	2×10^{-8}	2.11	1.63	0.48
9% GAC	4×10^{-8}	2.01	1.51	0.49
3% HDTMA-bentonite	2×10^{-8}	2.07	1.66	0.41
9% HDTMA-bentonite	2×10^{-7}	2.14	1.73	0.41
3% BTEA-bentonite	2×10^{-9}	2.13	1.75	0.38
9% BTEA-bentonite	2×10^{-8}	2.08	1.73	0.35
3% shale	5×10^{-9}	2.19	1.78	0.41
9% shale	1×10^{-9}	2.12	1.74	0.37

Note: Ave.=average; GAC=granular activated carbon; HDTMA-bentonite=hexadecyltrimethylammonium-bentonite; and BTEA-bentonite=benzyltriethylammonium-bentonite.

sociated with the amendments is due to the fact that the amendments have finer particle-size distributions than the Ottawa sand they replace.

Transport Simulations

Experimental results from permeability and sorption testing make it complicated to directly compare the effectiveness of the four proposed sorbents as amendments for clay liner systems. For example, shale exhibited the lowest sorptive capacity of all of the proposed amendments, but the permeability of specimens that included shale as a fraction of their composition yielded a hydraulic conductivity one to two orders of magnitude lower than conventional liner materials. Similarly, GAC exhibited a very large sorptive capacity for all organic solutes tested, however the permeability of specimens amended with this material had a comparable if not slightly larger permeability when compared to the other amendments. As a result, benzene transport simulations were performed in order to better evaluate the performance of these materials. Results from benzene transport simulations are presented in Table 7. Fig. 5 shows plots of mass of benzene exiting the liner per unit area as a function of time for shale, HDTMA-bentonite, and the unamended liner.

The predicted cumulative mass of benzene transported through the unamended liner was 3.0×10^3 mg over the 100-year simula-

Table 7. Simulation Results through Amended Liners

Amendment type	Cumulative mass (g)
Unamended	3.0×10^3
3% GAC	No mass
9% GAC	No mass
3% HDTMA-bentonite	2.65×10^3
9% HDTMA-bentonite	2.48×10^2
3% BTEA-bentonite	0.36×10^{-15}
9% BTEA-bentonite	No mass
3% shale	2.15×10^3
9% shale	1.32×10^2

Note: GAC=granular activated carbon; HDTMA-bentonite=hexadecyltrimethylammonium-bentonite; and BTEA-bentonite=benzyltriethylammonium-bentonite.

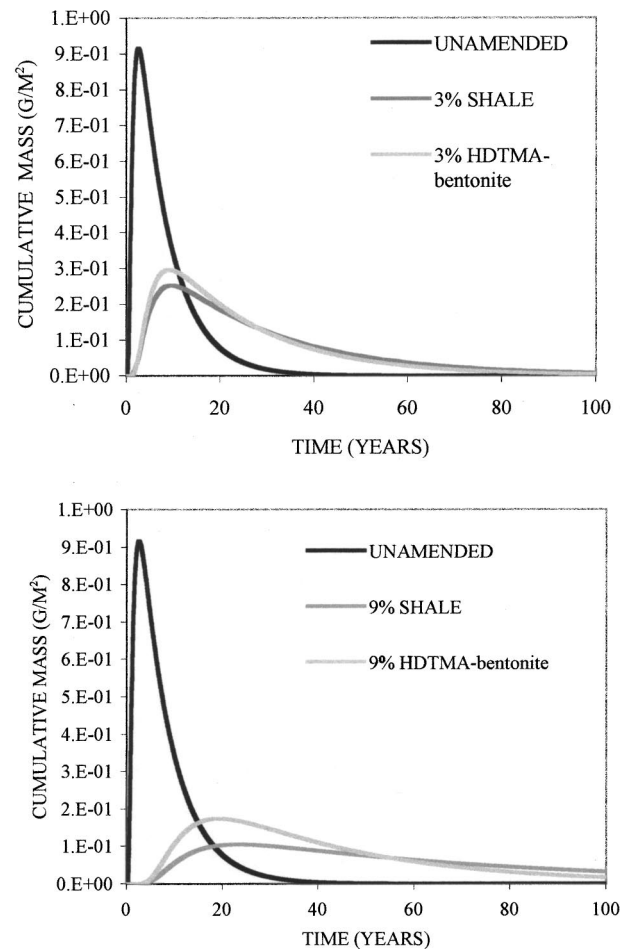


Fig. 5. Plots of mass of benzene per unit area exiting the liner versus time

tion period. Liners modified with shale and HDTMA-bentonite had a slight reduction in cumulative mass transported, however the most significant reduction in mass resulted from amending the liner with either BTEA-bentonite or GAC. Amending the liner with BTEA-bentonite at the 3% level resulted in a five-fold decrease in mass compared to the unamended case, while amending the liner with 9% BTEA-bentonite resulted in a hundred-fold decrease in mass transported through the liner. Modifying the liner with 3% GAC resulted in a decrease in mass of 7 orders of magnitude compared to the unamended liner, while modifying the liner with 9% GAC by weight resulted in essentially no pollutant mass exiting the liner over the entire 100-year simulation period. Although the liners amended with GAC had conductivity values equal to or slightly larger than the unamended liner, the increased sorptive capacity significantly retarded pollutant transport.

Conclusions

The measured sorption capacity of all amendments was greater than for conventional soil materials (Ottawa sand and untreated bentonite clay). For all three solutes, GAC exhibited the highest sorptive capacity, followed by BTEA-bentonite, HDTMA-bentonite, and then shale. GAC and BTEA-bentonite exhibited no competitive sorption effects between the three organic solutes and the synthetic leachate. Shale exhibited strong competitive effects

for benzene and TCE with the synthetic leachate present.

Hydraulic conductivity of specimens amended with either 3 or 9% amendment by weight met or surpassed regulatory requirements of 1×10^{-7} cm/s, with the exception of 3% GAC, which had a measured K value of 2×10^{-7} cm/s. There was little effect on permeability when the permeant fluid was changed to a synthetic leachate.

Transport simulations indicate that all modified liners performed better with regard to mitigating pollutant transport when compared to a conventional liner. The simulations indicate that liners modified with either BTEA-bentonite or GAC at either a 3 or 9% level (by weight) would minimize benzene transport through the liner over a 100-year period. The total mass of benzene transported through the liner was reduced only minimally when either HDTMA-bentonite or shale were incorporated into the liner. Although the total mass transported through liners modified with HDTMA-bentonite or shale is similar to the mass transported through the unamended liner, Fig. 5 indicates that the mass of benzene transported per unit area is significantly reduced when HDTMA-bentonite or shale is incorporated into the liner. It is also interesting to note that HDTMA-bentonite and shale performed similarly well, although HDTMA-bentonite has a significantly higher benzene sorption capacity than shale. The fact that benzene transport through the shale-amended liner was similar to that through the HDTMA-bentonite-amended liner may be attributed to the much lower permeability measured for the shale-amended specimens.

Acknowledgments

The writers thank Shawn Matott for his work in calibrating isotherm models to the sorption data, and Eric Anderson and Maryann Bogucki for aiding in the collection of laboratory data. Funding for one of the writers (S.B.-H.) was provided in part by the Department of Defense Graduate Research Fellowship Program, the Institute of Hazardous Materials Management, and the ARCS, Inc. Foundation.

References

- Bartelt-Hunt, S. L., Burns, S. E., and Smith, J. A. (2003). "Sorption of nonionic organic solutes to two organobentonites as a function of organic-carbon content." *J. Colloid Interface Sci.*, 266, 251–258.
- Bierck, B. R., and Chang, W. C. (1994). "Innovative solutions for contaminated waste site management." *Proc., Water Environ. Fed. Specialty Conf.*, Alexandria, Va., 461–472.
- Chiou, C. T. (1998). "Soil sorption of organic pollutants and pesticides." *Encyclopedia of environmental analysis and remediation*, Wiley, New York, Vol. 7, 4517–4554.
- Christensen, T. H., et al. (2001). "Biogeochemistry of landfill leachate plumes." *Appl. Geochem.*, 16, 659–718.
- Deitsch, J. J., Smith, J. A., Arnold, M. B., and Bolus, J. (1998). "Sorption and desorption rates of carbon tetrachloride and 1,2-dichlorobenzene to three organobentonites and a natural peat soil." *Environ. Sci. Technol.*, 32, 3169–3177.
- DiCesare, D., and Smith, J. A. (1994). "Effects of surfactants on the desorption rate on nonionic organic compounds from soil to water." *Rev. Environ. Contam. Toxicol.*, 134, 1–29.
- Gullick, R. W. (1998). "Effects of sorbent addition on the transport of inorganic and organic chemicals in soil-bentonite cutoff wall containment barriers." , Univ. of Michigan, Ann Arbor, Mich.
- Gullick, R. W., and Weber, W. J. (2001). "Evaluation of shale and organoclays as sorbent additives for low-permeability soil containment barriers." *Environ. Sci. Technol.*, 35, 1523–1530.
- Jaynes, W. F., and Boyd, S. A. (1991). "Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays." *Soil Sci. Soc. Am. J.*, 55, 43–48.
- Khandelwal, A., Rabideau, A. J., and Shen, P. (1998). "Analysis of diffusion and sorption of organic solutes in soil-bentonite barrier materials." *Environ. Sci. Technol.*, 32, 1333–1339.
- Manes, M. (1998). "Activated carbon adsorption fundamentals." *Encyclopedia of environmental analysis and remediation*, Wiley, New York, Vol. 1, 26–68.
- Matott, L. (2004). *IsoFit documentation and user's guide, version 1.0*, Dept. of Civil, Structural, and Environmental Engineering, Univ. at Buffalo, Buffalo, N.Y.
- Montgomery, J. H., ed. (1996). *Groundwater chemicals desk reference*, 2nd Ed., Lewis, New York.
- Mott, H. V., and Weber, W. J. (1992). "Sorption of low molecular weight organic contaminants by fly ash: Considerations for the enhancement of cutoff barrier performance." *Environ. Sci. Technol.*, 26, 1234–1242.
- Park, J. K., and Nibras, M. (1993). "Mass flux of organic chemicals through polyethylene geomembranes." *Water Environ. Res.*, 65, 227–237.
- Quigley, R. M., Fernandez, F., and Rowe, R. K. (1988). "Clayey barrier assessment for impoundment of domestic waste leachate (southern Ontario) including clay-leachate compatibility by hydraulic conductivity testing." *Can. Geotech. J.*, 25(B), 574–581.
- Rabideau, A. J. (2003). *MOUSER version 1: Moderately user-friendly reactive transport model*, Dept. of Civil, Structural, and Environmental Engineering, Univ. at Buffalo, Buffalo, N.Y., public domain software and manual distributed at www.groundwater.buffalo.edu, updated 2001.
- Rabideau, A. J., and Khandelwal, A. (1998). "Nonequilibrium sorption in soil/bentonite barriers." *J. Environ. Eng.*, 124(4), 329–335.
- Rakhshandehroo, G. R., Wallace, R. B., Boyd, S. A., and Voice, T. C. (1998). "Hydraulic characteristics of organomodified soils for use in sorptive zone applications." *Soil Sci. Soc. Am. J.*, 62, 5–12.
- Rowe, K. R., and Booker, J. R. (1985). "One-dimensional pollutant migration in soils of finite depth." *J. Geotech. Eng.*, 111(4), 479–499.
- Shackelford, C. D. (1991). "Laboratory diffusion testing for waste disposal—A review." *J. Contam. Hydrol.*, 7, 177–217.
- Smith, J. A., and Galan, A. (1995). "Sorption of nonionic organic contaminants to single and dual organic cation bentonites from water." *Environ. Sci. Technol.*, 29, 685–692.
- Smith, J. A., and Jaffé, P. R. (1994). "Benzene transport through landfill liners containing organophillic bentonite." *J. Environ. Eng.*, 120(6), 1559–1577.
- Smith, J. A., Jaffé, P. R., and Chiou, C. T. (1990). "Effect of ten quaternary ammonium cations on tetrachloromethane sorption to clay from water." *Environ. Sci. Technol.*, 24, 1167–1172.
- Smith, J. A., Witkowski, P. J., and Chiou, C. T. (1988). "Partition of nonionic organic compounds in aquatic systems." *Rev. Environ. Contam. Toxicol.*, 39, 465–473.
- U.S. Environmental Protection Agency (EPA). (2000). "Evaluation and characterization of landfill leachates." Draft Report submitted by Science Applications International Corporation, Reston, Va.